



Inhibition of activated sludge respiration by sodium azide addition: Effect on rheology and oxygen transfer

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ARTICLE INFO

Article history:

Received 4 April 2010

Received in revised form 16 July 2010

Accepted 21 July 2010

Keywords:

Oxygen transfer

K_La

Rheology

Sodium azide

Activated sludge

ABSTRACT

Although microorganism respiration inhibition by sodium azide (NaN_3) is used in some studies to identify activated sludge adsorption capacity, little is known about the effect of this compound on the suspension properties. In this study we have investigated the effect of NaN_3 addition on both volumetric oxygen mass transfer coefficient and rheology of activated sludge (AS) suspensions in a 1.9 L bioreactor. The rheological properties (shear thinning one) of AS suspensions with and without NaN_3 addition are measured *in situ* (triphasic conditions). It appears that NaN_3 addition leads to a deflocculation of AS suspensions and thus a decrease in apparent viscosity. A small amount of suspended solids was added in order to obtain identical apparent viscosities (under 1.2 or 46.3 s^{-1}) for AS suspensions with and without NaN_3 addition. K_La values were then measured in both respiring and non-respiring suspensions for different air flow rates (2, 3 or 4 L/min) and under low or high mechanical shear rate (1.2 or 46.3 s^{-1}). Results show that under high mechanical shear rate, the respiration state for a given air flow rate does not impact the K_La values. On the contrary, under low mechanical shear rate, NaN_3 addition induces an increase of K_La values in comparison with those obtained with the respiring biomass. This effect, for a same apparent viscosity, is attributed to the deflocculation observed in the presence of NaN_3 . Indeed, AS with and without NaN_3 addition used for the K_La measurements induce a modification of the floc internal structure, corresponding to smaller floc size in the case of NaN_3 addition.

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1. Introduction

It is not necessary to present the classical activated sludge (CAS) process, given its wide use for the biological treatment of municipal effluents. However, in front of the emergence of new contaminants such as pharmaceutical compounds or personal care products not degraded during CAS treatment, Membrane BioReactors (MBR) appear as a possible solution. MBRs gather a longer sludge retention time and a higher biomass concentration compared to CAS. These advantages might be beneficial to the biodegradation of refracting compounds. Some studies highlight the better removal efficiency of some pharmaceuticals compounds, endocrine disrupters, fragrances and surfactants by MBR compared to CAS [1–4]. In spite of the advantages of MBR in terms of effluent quality, this process remains more costly. One of the main costs concerns the membrane filtration, which has an impact on both capital and operating expenditure. The development of membrane technologies allowed this cost to decrease during the last two decennia. The biomass aeration represents another important portion of the operating cost. The

biodegradation efficiency, indeed, strongly depends on the oxygen supply to the bacteria, since the kinetic of aerobic biodegradation is conditioned by the oxygen transfer from the gas phase to the microorganisms [5]. Consequently, the optimisation of the oxygen transfer is a key to a better utilization of biological wastewater treatment plants.

In MBR, optimizing the transfer is more challenging than in the CAS process. The high biomass concentration (10–15 g/L) leads to an increase of apparent viscosity and a decrease of turbulence, both having for consequence a decrease of the volumetric oxygen mass transfer coefficient, K_La . Most of broth suspensions show, as activated sludge, a non-Newtonian rheological behaviour with shear-thinning properties. The literature correlations to calculate the K_La usually gather parameters such as the gas superficial velocity, the agitation power density, and the suspension apparent viscosity [6]. However, the latter is always measured *ex situ*, and consequently do not take into account the decrease of apparent viscosity induced by the presence of air plume. Seyssieq et al. [6] observed a decrease of apparent viscosity under low mechanical shear rates (0.408–4.76 rpm corresponding shear rates of 0.34–3.97 s^{-1}) as air flow rate is increased. On the contrary, in the high mechanical shear region (40.8–75.4 rpm and shear rates of 34–62.84 s^{-1}), the apparent viscosity value becomes independent

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of the air flow rate, whatever its value from zero (un-aerated diphasic suspension) to 3 L/min (aerated triphasic suspensions). This phenomenon is linked to the shear thinning properties of activated sludge suspensions via the configuration bioflocs take under different hydrodynamic conditions [6]. Under low mechanical stirring, the configuration of bioflocs is only driven by the shear rate induced by the air plume. An increase of the air flow rate induces an increase of the shear due to bubbles injection, leading to a decrease in apparent viscosity (shear thinning medium). Conversely under high mechanical stirring, the mechanical shear rate becomes far prevailing from the air plume one and imposes hydrodynamic conditions in the bioreactor. In that case, whatever the presence or absence of air injection the apparent viscosity is constant for a given mechanical shear rate. Consequently, in the liquid side of the interface the non-Newtonian viscosity of the suspension itself is modified in the presence of air under low mechanical agitation.

Moreover, even though an extensive research on $K_L a$ in different fluids and suspensions is presented in the literature, only a few publications deal specifically with activated sludge at high total suspended solids [7–10]. These studies present an identical result. The suspended solids concentration is one of the main, if not the main parameter controlling the oxygen transfer.

In the present work, oxygen transfer in activated sludge at high concentration is investigated in a mechanically agitated bioreactor. The effect of the physical presence of the flocs on the transfer is comprehended by measuring the volumetric oxygen mass transfer coefficient in the respiring suspension and comparing it with the measurement when the respiration is inhibited. The addition of an inorganic compound, sodium azide, to the suspension theoretically permits the oxygen transfer to be studied with a model fluid that retains the complexity of activated sludge (porous flocs as particulate matter). The impeller is connected to a rheometer and allows the determination of apparent viscosity *in situ*, i.e. when the suspension is aerated. The influence of operating conditions such as air flow rate and impeller speed is also discussed.

2. Materials and methods

2.1. Activated sludge

The activated sludge (AS) came from an urban wastewater treatment plant (Aix-en-Provence, France, 175,000 eq. inh., 35,000 m³/d). The samples were taken from the recirculation loop between the aeration basins and the secondary clarifier. The initial total suspended solids (TSS) concentration varied from 2 to 4.5 g/L. The amount of volatile suspended solids ranged from 77% to 80% for all the experiments. The AS was concentrated by gravimetric filtration using paper filters (average size of pores around 100 μm) in order to obtain a TSS content of about 15 g/L. This concentration corresponds to the average concentration generally used in membrane bioreactors for wastewater treatment. Before any experiment was performed, sludge was aerated and oxygen uptake rate (OUR) of small samples was monitored until endogenous respiration was reached.

2.2. Bioreactor and rheological devices

The set-up used in this study (Fig. 1) was composed of a bioreactor equipped with a double helical ribbon impeller (HRI). The impeller had a diameter and height of 9.5 cm each, while the bioreactor was 12 cm in diameter. A volume of 1.9 L of activated sludge was aerated by compressed air through a porous membrane. The compressed air pipe was equipped with a flowmeter and a valve to control the air flow rate. Water was circulated in a double envelope to maintain the sludge temperature constant at 20 ± 0.2 °C. A

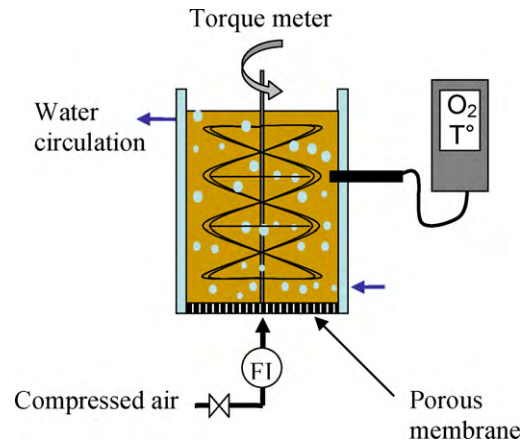


Fig. 1. Schematic representation of the experimental device.

dissolved oxygen probe was fixed perpendicular to the air flow to avoid any air bubble deposition on the surface of the probe. This probe allowed both OUR and $K_L a$ measurements (see Section 2.3).

To perform the *in situ* viscosity curves determination of AS suspensions (with or without aeration), the HRI of the bioreactor was connected to a shear rate imposed rheometer (Rheomat 30, Contraves) with 30 available values of the imposed rotation speed in the range 0.408–257 rpm. The stirring torque was measured for each value of the rotation speed.

Before each torque measurement, the suspension was pre-sheared at the maximum rotation speed for 30 s to insure its homogeneity. The rotation speed was then decreased to the desired value and the torque was recorded for 15 s after 15 s of stabilization.

Calculations of the *in situ* viscosities were performed using the Metzner-Otto's principle. It defines an apparent viscosity η_a (Pa s) based on the generalization for non-Newtonian media of the relation existing in an agitated vessel (in the laminar region) between the dimensionless power N_p and the Reynolds number Re (Eq. (1))

$$N_p = \frac{P}{\rho N^3 d^5} = \frac{K_p}{Re} = \frac{K_p \eta_a}{\rho N d^2} \quad \text{then} \quad \eta_a = \frac{P}{K_p N^2 d^3} \quad (1)$$

where P (W) is the mechanical agitation power related to the agitation torque C (Nm) and to the mechanical rotation rate N (s⁻¹) by the following equation:

$$P = 2\pi NC \quad (2)$$

K_p corresponds to the laminar power curve constant and d (m) to the impeller diameter.

At a rotation rate N corresponds an effective shear rate $\dot{\gamma}_{MO}$ (s⁻¹) related to the rotation speed of the impeller by the Metzner-Otto dimensionless constant characterising the stirrer geometry (Eq. (3))

$$\dot{\gamma}_{MO} = K_{MO} N \quad (3)$$

Values of K_p and K_{MO} constants have been determined at respectively 393 and 50. Details of the calibration can be found in the work published by Seyssiecq et al. [6].

Some viscosity measurements were also performed *ex situ* (without aeration), after sampling small quantities of suspension from the bioreactor. A rheometer (AR550, TA Instrument), equipped with a single helical ribbon impeller of 28 mm in diameter has been used. The stator diameter was 30 mm and the sample volume was 36 mL.

2.3. Rheological model

In the rheological part of this study, the Ostwald power law model (Eq. (4)) has then been used to represent the viscosity curves

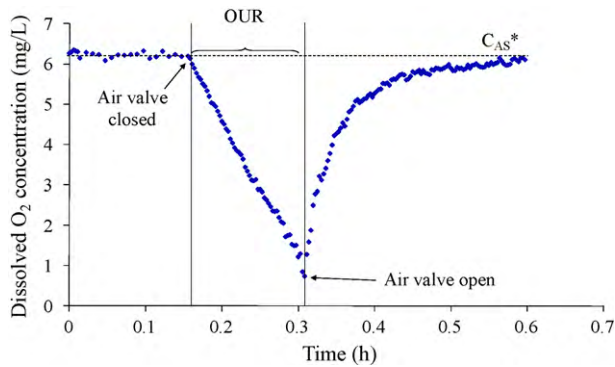


Fig. 2. Dissolved oxygen concentration profile versus time during an OUR- K_La test [TSS 15.7 g/L, air flow rate 3 L/min].

of rough AS and AS with sodium azide addition suspensions.

$$\tau = K\dot{\gamma}^n \quad (4)$$

The two parameters of this model, i.e. the consistency index (K in Pa s^n) and flow index (n) have been calculated using a simple linear regression in log–log scale.

2.4. Oxygen transfer measurements: K_La and OUR

The dissolved oxygen concentration was measured by an oxymeter HQ30D (Hach Lange), equipped with a temperature sensor. Compressed air was introduced in the media through the porous membrane at a chosen flow rate until stabilization of dissolved oxygen (DO) concentration in the liquid phase was reached as a result of equilibrium between oxygen dissolution at 20 °C and microorganisms respiration. Air injection was then stopped and decreasing values of the DO concentration were recorded every 10 s to calculate the OUR, as the slope of the linear decrease of DO concentration versus time. When DO concentration reached about 2 mg/L, the air valve was open again and increasing values of DO concentration were also recorded every 10 s. The volumetric oxygen mass transfer coefficient (K_La) is calculated based on the classical mass balance of DO in a biological media (Eq. (5))

$$\frac{dC}{dt} = K_La(C^* - C) - \text{OUR} \quad (5)$$

where C is the DO concentration and C^* the saturation DO concentration.

When the steady state between the oxygen dissolution and the respiration is reached, this mass balance becomes:

$$K_La(C^* - C_{eq}) = \text{OUR} \quad (6)$$

where C_{eq} is the steady state equilibrium DO concentration.

Eq. (5) can be recombined into:

$$\frac{dC}{dt} = K_La(C_{eq} - C) \quad (7)$$

The K_La value can thus be calculated by integration of Eq. (7) during the reoxygenation phase. Fig. 2 presents an example of a dissolved oxygen profile obtained during this procedure.

As the apparent viscosity is known to impact on the oxygen transfer in the bioreactor, two rotation speeds have been chosen for K_La measurement based on the viscosity curves shown in Fig. 3 for different air-flow rate: a low value of 1.39 rpm ($\dot{\gamma}_{MO} = 1.2 \text{ s}^{-1}$) for which air injection has the main influence on apparent viscosity and a high value of 55.5 rpm ($\dot{\gamma}_{MO} = 46.3 \text{ s}^{-1}$) for which the apparent viscosity only depends on the mechanical shear rate.

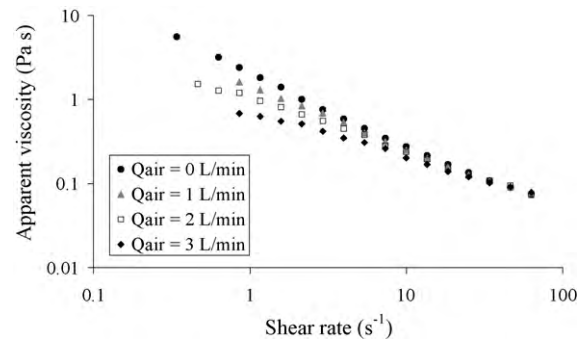


Fig. 3. *In situ* viscosity curves at different air flow rate [TSS = 14.8 g/L].

2.5. Respiration inhibition

An inhibition of the biomass respiration (blockage of the ATP synthesis) is known to be obtained by addition of the appropriate quantity of sodium azide (NaN_3) (99%, Acros organics, Noisy-le-Grand, France) [11]. This optimal quantity depends on the biomass solid concentration and, for a given biomass first needs to be determined experimentally. For this purpose, various amounts of NaN_3 were added to AS suspensions at 15 g/L in TSS, while monitoring OUR values over time. In Fig. 4, the obtained drop in OUR has been reported in percentage, for times between 12 and 18.5 h after the addition of NaN_3 . We observed that, in the case of the activated sludge used in this work, a maximum state of inhibition of the microorganisms respiration was obtained after addition of NaN_3 for concentrations $\geq 0.2 \text{ g/g}_{\text{TSS}}$. In the experimental part of this study, mass concentration of NaN_3 at $0.2 \text{ g/g}_{\text{TSS}}$ was thus used in order to obtain a non-respiring “inert” biological suspension, to distinguish between physical and biological (respiration) effects on the K_La value.

Working at the optimum NaN_3 concentration, 18 h after the NaN_3 addition, glucose was added to the broth, to determine if the respiration was completely inhibited or not. Five hours after the addition, glucose concentration in the liquid phase was measured to see if any biodegradation of this substrate had occurred. A complete absence of glucose biodegradation is observed, corresponding to a total and irreversible state of inhibition of the biomass respiration for a NaN_3 addition at $0.2 \text{ g/g}_{\text{TSS}}$. However, 18 h after NaN_3 addition, the suspension had a high tendency to foam when aerated, which led to a biomass loss and difficulties to perform the rheological measurements. Consequently attention was focused on the evolution of the percentage of drop in OUR value during the very first times (first 4 h) following the addition of NaN_3 , when foam had not formed yet (Fig. 5). We could observe that the drop in OUR value is important during the first 3 h while its value remains stable after

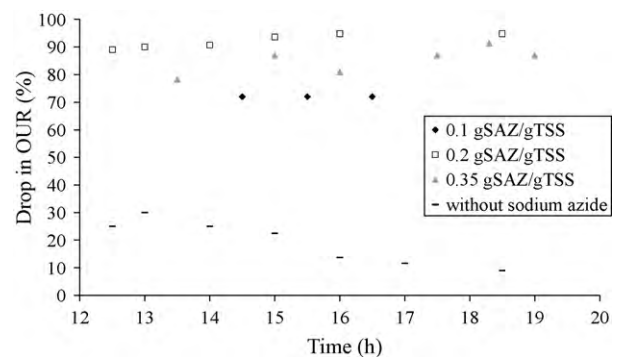


Fig. 4. Variation of OUR drop versus time depending on sodium azide concentration.

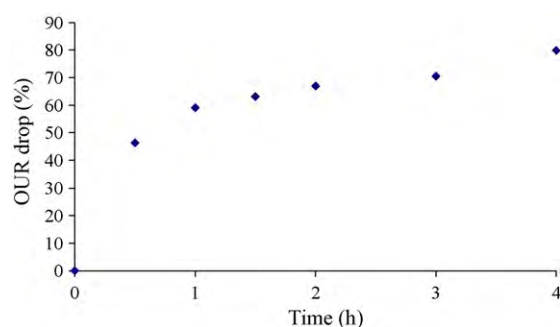


Fig. 5. Variation of early OUR drop versus time after sodium azide addition ($0.2 \text{ g}_{\text{NaN}_3}/\text{g}_{\text{TSS}}$).

3 h, corresponding to a drop in OUR of at least two third of its initial value.

2.6. Analytical methods

TSS were measured by centrifugation of a 30 mL sludge sample for 15 min at 15000 rpm followed by drying the pellet at 105°C until a constant weight was obtained (24 h). TVSS were measured after 2 h at 550°C .

The degree of sludge deflocculation was estimated using the method presented by Wilén et al. [12]. Samples of sludge were taken from the bioreactor and centrifuged at $1300 \times g$ for 2 min. Supernatant turbidity was then measured as the absorbance at 650 nm.

3. Results and discussion

3.1. Effect of sodium azide addition on the rheological behaviour of AS suspensions

Apparent viscosity measurements have also been performed to determine a possible effect of NaN_3 addition resulting in a respiration inhibition, on the rheology of the broth. Two litres of the resulting suspension were concentrated at TSS of 14 g/L. The AS was separated in two samples of 1 L each. One sample was used as a reference and simply put under aeration in a bioreactor, under an air-flow rate of 3 L/min. NaN_3 ($0.2 \text{ g}/\text{g}_{\text{TSS}}$) was added to the second sample of AS then put under identical aeration conditions. Fig. 6 represents the apparent viscosity curves obtained with the *ex situ* AR550 rheometer (no air added during measurements) for these suspensions. Comparison is made between the initial sludge and the two sludge samples 24 h after NaN_3 addition. Without sodium azide addition, the apparent viscosity curve does not change significantly in 24 h. On the contrary, the addition of NaN_3 induces

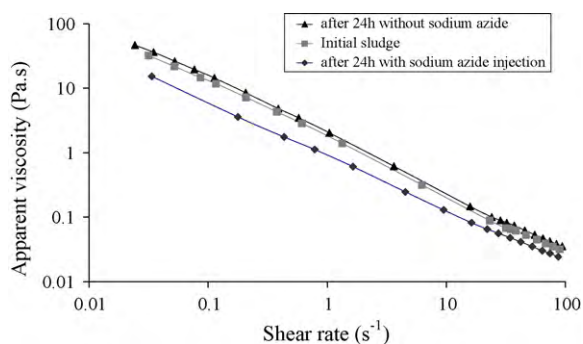


Fig. 6. *Ex situ* apparent viscosity curves with and without injection of sodium azide [TSS = 14 g/L].

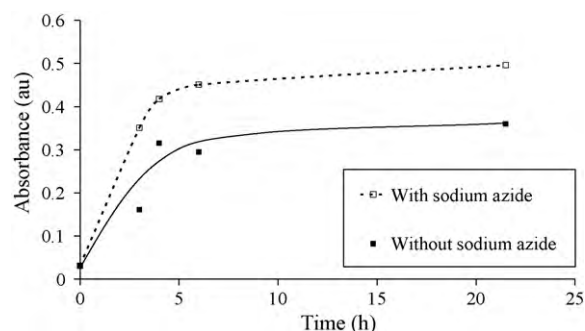


Fig. 7. Absorbance of supernatant versus time with and without sodium azide [TSS = 14 g/L; $[\text{NaN}_3] = 0.2 \text{ g}/\text{g}_{\text{TSS}}$].

a decrease of apparent viscosity, the whole viscosity curve being shifted downwards. The Ostwald parameters calculation indicates a decrease of the shear thinning level of this suspension. Indeed, the biomass respiration inhibition due to NaN_3 addition leads to a decrease of 53% of the consistency index K (from 1.66 to 0.89 Pa s^n) while the flow index n increases from 0.11 to 0.18.

The variations of supernatant absorbance with time (Fig. 7) were also monitored on the samples previously described. Absorbance increases with time regardless of the sludge sample (with or without NaN_3). This reveals a certain deflocculation degree of all suspensions with aging. However, bioflocs in contact with NaN_3 are subjected to a higher deflocculation degree, as shown by the higher absorbances obtained in presence of NaN_3 . Concerning the rough AS suspensions, the observed deflocculation is simply due to the natural aging of the biomass undergoing a 24 h starvation under aeration. Indeed, it is well known that during a period of starvation, sludge flocs strength decreases. In their study on the rheological behaviour of activated sludge (TSS = 43 g/L), Mori et al. [13] underlined a decrease in both viscoplastic and shear-thinning properties after 4 days of starvation. This observation seems to be correlated with a decrease in concentration of adsorbed exopolysaccharides (EPS) in bioflocs. In the case of this study, after 24 h of starvation, the bioflocs strength does not seem to be sufficiently modified to induce significant variations of the rheological properties of the sludge. We can hypothesize that, during rheological measurements, under the shear field induced by the helical ribbon impeller (low shearing impeller), flocs size does not change significantly between the initial AS and the 24 h aged AS. However, under the conditions prevailing during the preparation of the supernatant samples before the deflocculation degree determination, there is a centrifugation step of the suspension. During this step, the compression induced by the centrifugal force can break the bioflocs weakened by starvation. This leads to a release of small particles in the supernatant and thus to a subsequent increase in turbidity. Concerning the AS with NaN_3 addition, the microorganisms have to face a 24 h period of starvation coupled with a decrease of the aerobic activity. This leads to a much more important decrease of flocs strength than the one observed with the 24 h aged rough AS. Bioflocs of this suspension are submitted to an important breakage during the centrifugation step, leading to higher turbidity values of their supernatant compared to the one of rough AS. During the rheological measurements, the non-respiring bioflocs obtained in the presence of NaN_3 are shown to form a less shear thinning suspension than the rough sludge. This is linked to the presence of bioflocs of smaller size in the case of NaN_3 addition than in the case of the initial AS. Indeed, the deflocculation induced by the inhibition of the respiration corroborates the change of the Ostwald parameters. The decrease of K and the increase of n , and thus the decrease of apparent viscosity can be explained by the breakage of part of the bacterial flocs structure, leading to a release of water molecules

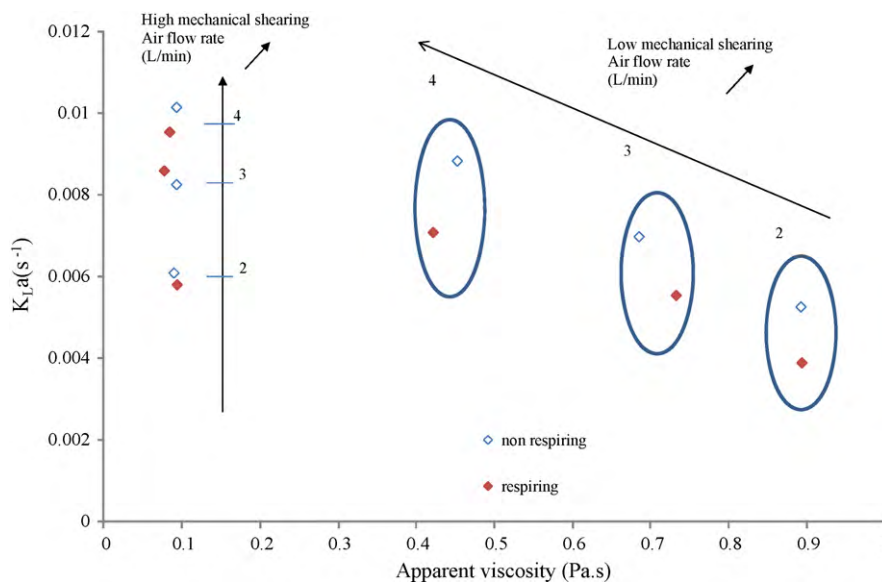


Fig. 8. Variation of $K_L a$ versus apparent viscosity with and without respiration [Viscosity measured *in situ*, air flow rate equal to 2, 3 and 4 L/min; shear rate equal to 1.2 and 46.3 s^{-1}].

previously trapped inside the flocs. An increase of the flowing properties of the suspension (decrease in shear thinning properties) is then observed [14].

3.2. Effect of operating conditions on the oxygen transfer

The main goal of the experiments conducted on oxygen mass transfer measurements is to determine the effect of biomass respiration on the $K_L a$ value, by comparing $K_L a$ obtained with rough AS and AS with sodium azide addition. However, since the NaN_3 addition has been shown to have a non-negligible effect on the AS apparent viscosity, it has been decided to add a small amount of concentrated sludge to obtain, after reaction with NaN_3 , an apparent viscosity close to its initial value. A volume of 300 mL of AS was concentrated at a TSS around 25 g/L. The respiration inhibition of this sample was also performed by adding NaN_3 . The average quantity of TSS added to the bioreactor after reaction with the sodium azide was equal to 0.4 g/L. The TSS variation was thus negligible considering the initial concentration of 15 g/L. The volume of sludge was maintained constant at 1.9 L.

Volumetric oxygen mass transfer coefficient values have been determined at different air flow rates (2, 3 and 4 L/min) and under the high and low agitation rates mentioned in Section 3.1. $K_L a$ values obtained with both respiring and non-respiring biomass are plotted versus the apparent viscosity of the broth in Fig. 8. Values on the left correspond to those obtained for a high mechanical shear rate ($\dot{\gamma} = 46.3 \text{ s}^{-1}$), while the values on the right correspond to a low mechanical shear rate ($\dot{\gamma} = 1.2 \text{ s}^{-1}$). The variations of the oxygen transfer coefficient are consistent with the variations previously presented in the literature. $K_L a$ values increase while increasing both the stirring rate (decrease of apparent viscosity on the graph) and the air flow rate. The increase of agitation rate first improves the mass transfer through the liquid phase (increase of K_L), notably due to the decrease in apparent viscosity of the shear thinning suspension. In addition, the increase of stirring rate enhances the interfacial exchange area (increase of a) through a decrease of the mean air bubble diameter. Both effects induce an increase of the global oxygen transfer coefficient as the mechanical shearing is increased. Concerning the effect of the air flow rate on the $K_L a$ values, under high mechanical shear rate, we observe an increase of $K_L a$ with air flow rate which is usually explained as an

increase of the gas hold-up and of the oxygen concentration gradient. Under low mechanical stirring, an increase of air flow rate still induces an increase of $K_L a$ values. However, the latter is not only due to the previously cited effects but also to a decrease in apparent viscosity. Indeed, Fig. 3 shows that, under low mechanical shearing, there is a shear thinning behaviour of AS suspension due to the shearing forces of rising air bubbles. As a consequence, in this case, the decrease of viscosity of the media due to the shearing of air plume also contributes to enhance the oxygen transfer. This additional effect does no more appear under high stirring for which the apparent viscosity of the AS is mainly driven by mechanical shearing forces, as the shear induced by the air bubbles is negligible.

The influence of NaN_3 addition on the volumetric oxygen transfer coefficient depends on the stirring rate of the impeller. Under high shear rate, the apparent viscosity is not affected by the increase of air flow rate (the small difference only comes from the use of AS sampled at different dates). Consequently, $K_L a$ values are on a same vertical line (corresponding to a same abscissa, i.e. viscosity). The only effect leading to an increase in $K_L a$ values is the increase in air flow rate (increase in gas hold-up and oxygen concentration gradient). No effect of the respiration of microorganisms on the oxygen transfer rate can be seen under high mechanical shear rate, since $K_L a$ values are very close for either respiring or non-respiring biomass at an identical air flow rate. This implies that the oxygen transfer through the liquid phase is nor increased nor decreased by the biomass respiration.

Encircled values correspond to the low mechanical shear rate ($\dot{\gamma} = 1.2 \text{ s}^{-1}$). As previously explained, in this case, an increase of the air flow rate both induces a reduction in apparent viscosity and an increase of $K_L a$ values. This explains why in Fig. 8, $K_L a$ values corresponding to the low mechanical shear rate are plotted along an inclined line.

In this case, whatever the air flow rate, $K_L a$ values measured in a non-respiring biomass (empty symbols) are significantly higher than values measured when the microorganisms are under endogenous respiration (full symbols).

The addition of NaN_3 to inhibit the respiration first induces a decrease in apparent viscosity (Fig. 6) due to a deflocculation of bacterial flocs structure. As previously explained, this effect was compensated in terms of viscosity by a small addition of concentrated biomass (3% in mass). However, even if this non-respiring

suspension has the same viscosity than the respiring AS, it is important to underline that this viscosity is obtained with bioflocs of smaller size (due to the deflocculation induced by NaN_3 addition).

The increase of K_La can thus be interpreted as an effect of the change in the configuration and size of the flocs. In the case of the deflocculated biomass, the oxygen transfer through the liquid phase is enhanced compared to the one obtained with strongly flocculated microorganisms.

Galaction et al. investigated the oxygen mass transfer in four non-respiring biomass suspensions and identified different oxygen transfer rate depending on the morphological characteristics of the microorganisms [15]. Other studies have also been underlined that the mechanical shear induces AS floc size evolution [16,17]. In the case of experiments conducted under high shearing rate, we can hypothesize that AS suspensions exhibit the same floc size distribution with and without azide injection (floc size only dependent on mechanical forces), leading to identical oxygen mass transfer rate.

4. Conclusion

The effect of sodium azide on concentrated activated sludge (TSS 15 g/L) was investigated in terms of rheological behaviour and oxygen transfer capacity. The following conclusions can be drawn:

1. Sodium azide is effective to inhibit the biomass respiration and metabolism for an activated sludge suspension; an optimum concentration was found at 0.2 g/g_{TSS}.
2. As concerns the rheological characterisation, the activated sludge exhibits a non-Newtonian shear thinning behaviour with and without sodium azide injection. However, the reaction with sodium azide induces a decrease of the apparent viscosity, due to a deflocculation of the biological suspension.
3. Under low mechanical shear rate, inhibition of biological activity of activated sludge leads to an increase of K_La values, probably due to the deflocculation phenomenon described at point 2, even though the viscosity of the suspension was kept at a constant value (smaller flocs sizes). On the other hand, under high shear rate, the flocculation state of the suspension is only driven by mechanical forces. K_La values are independent of the respiration state of microorganisms.

This work emphasizes the importance of measuring the viscosity *in situ*, i.e. in the presence of aeration, when measuring volumetric oxygen transfer coefficients. In future works, the “*in situ*” apparent viscosity will be integrated into a correlation for

K_La calculation. Additionally, it appears that sodium azide leads to a destabilisation of the flocs and as a consequence a change of viscosity and oxygen transfer rate. It is likely to think that the deflocculation induced by NaN_3 addition can also have an influence on other physical–chemical properties of the flocs, such as sorption capacities.

References

- [1] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, *Water Res.* 43 (3) (2009) 831–841.
- [2] S. Weiss, T. Reemtsma, Membrane bioreactors for municipal wastewater treatment—a viable option to reduce the amount of polar pollutants discharged into surface waters? *Water Res.* 42 (14) (2008) 3837–3847.
- [3] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, *Water Res.* 39 (19) (2005) 4797–4807.
- [4] S. González, M. Petrovic, D. Barceló, Removal of a broad range of surfactants from municipal wastewater—comparison between membrane bioreactor and conventional activated sludge treatment, *Chemosphere* 67 (2) (2007) 335–343.
- [5] B. Marrot, A. Barrios Martinez, P. Moulin, N. Roche, Experimental study of mass transfers (aeration and membrane separation) in a membrane bioreactor, *Eng. Life Sci.* 5 (5) (2005) 409–414.
- [6] I. Seyssiecq, B. Marrot, D. Djerroud, N. Roche, In situ triphasic rheological characterisation of activated sludge, in an aerated bioreactor, *Chem. Eng. J.* 142 (1) (2008) 40–47.
- [7] J. Krampe, K. Krauth, Oxygen transfer into activated sludge with high MLSS concentrations, *Water Sci. Technol.* 47 (11) (2003) 297–303.
- [8] P. Cornel, M. Wagner, S. Krause, Investigation of oxygen transfer rates in full scale membrane bioreactors, *Water Sci. Technol.* 47 (11) (2003) 313–319.
- [9] E. Germain, F. Nelles, A. Drews, P. Pearce, M. Kraume, E. Reid, S.J. Judd, T. Stephenson, Biomass effects on oxygen transfer in membrane bioreactors, *Water Res.* 41 (5) (2007) 1038–1044.
- [10] J. Henkel, M. Lemac, M. Wagner, P. Cornel, Oxygen transfer in membrane bioreactors treating synthetic greywater, *Water Res.* 43 (6) (2009) 1711–1719.
- [11] K. Xu, W.F. Harper Jr., D. Zhao, 17[alpha]-Ethinylestradiol sorption to activated sludge biomass: thermodynamic properties and reaction mechanisms, *Water Res.* 42 (2008) 3146–3152.
- [12] B.M. Wilén, K. Keinding, P.H. Nielsen, Flocculation of activated sludge flocs by stimulation of the aerobic biological activity, *Water Res.* 38 (2004) 3909–3919.
- [13] M. Mori, J. Isaac, I. Seyssiecq, N. Roche, Effect of measuring geometries and of exocellular polymeric substances on the rheological behaviour of sewage sludge, *Chem. Eng. Res. Des.* 86 (2008) 554–559.
- [14] G. Guibaud, P. Dollet, N. Tixier, C. Dagot, M. Baudu, Characterisation of the evolution of activated sludges using rheological measurements, *Process Biochem.* 39 (11) (2004) 1803–1810.
- [15] A.-I. Galaction, D. Cascaval, C. Oniscu, M. Turnea, Prediction of oxygen mass transfer coefficients in stirred bioreactors for bacteria, yeasts and fungus broths, *Biochem. Eng. J.* 20 (1) (2004) 85–94.
- [16] V. Chaignon, B.S. Lartiges, A. El Samrani, C. Mustin, Evolution of size distribution and transfer of mineral particles between flocs in activated sludges: an insight into floc exchange dynamics, *Water Res.* 36 (3) (2002) 676–684.
- [17] G.P. Sheng, H.Q. Yu, X.Y. Li, Stability of sludge flocs under shear conditions, *Biochem. Eng. J.* 38 (3) (2008) 302–308.